
REPORT No. 280

**THE GASEOUS EXPLOSIVE REACTION
THE EFFECT OF INERT GASES**

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SUMMARY

(1) Attention is called in the following paper to previous investigations of gaseous explosive reactions carried out under constant-volume conditions, where the effect of inert gases on the thermodynamic equilibrium was determined. The advantage of constant-pressure methods over those of constant volume as applied to studies of the gaseous explosive reaction is pointed out and the possibility of realizing for this purpose a constant-pressure bomb mentioned.

(2) The application of constant-pressure methods to the study of gaseous explosive reactions, made possible by the use of a constant-pressure bomb, led to the discovery of an important kinetic relation connecting the rate of propagation of the zone of explosive reaction within the active gases, with the initial concentrations of those gases:

$$s = k_1[A]^{n_1}[B]^{n_2}[C]^{n_3} \text{-----}$$

(3) By a method analogous to that followed in determining the effect of inert gases on the equilibrium constant, K , the present paper records an attempt to determine their kinetic effect upon the expression given above. It is found that this effect for the inert gases investigated, — N_2 , He , and CO_2 —may be expressed as

$$s = k_1[A]^{n_1}[B]^{n_2}[C]^{n_3} \text{-----} + \beta[G_i]$$

where $[G_i]$ represents the initial concentration of the inert gas. From results obtained it seems probable that the value of β depends upon the combined effect of the thermal properties of the inert gas on the heat distribution of the reaction; the property of heat conductivity being predominant.

(4) An example of the utility of the constant-pressure bomb for the study of the kinetics of the gaseous explosive reaction is offered in the results of the present paper.

THERMODYNAMICS

From the standpoint of thermodynamics the effect of inert gases upon the equilibrium of the gaseous explosive reaction has received extended consideration from Nernst and his pupils (References 1, 2, 3), who employed in their investigations a spherical bomb of constant volume fired from the center. This series of investigations extended to temperatures of over 3,000° Abs. and formed part of the most extensive investigation of a gaseous reaction involving the equilibrium products of combustion, carbon dioxide, and water vapor, that has yet been carried out. "No other chemical equilibrium has so far been investigated by so many methods which can also be controlled at the same time by thermodynamic calculations. * * * A specially high value must be attached to explosion methods, since, by suitable variations of the experimental conditions it enables both the specific heats and the equilibrium to be determined." (Reference 4.)

In a previous report (Reference 5), a simple device was described that was found to function as a bomb of constant pressure. This simple device—an ordinary soap film holding temporarily the active gases to be investigated—provides the complement to the bomb of constant volume in the relation

$$PV = nRT \quad (1)$$

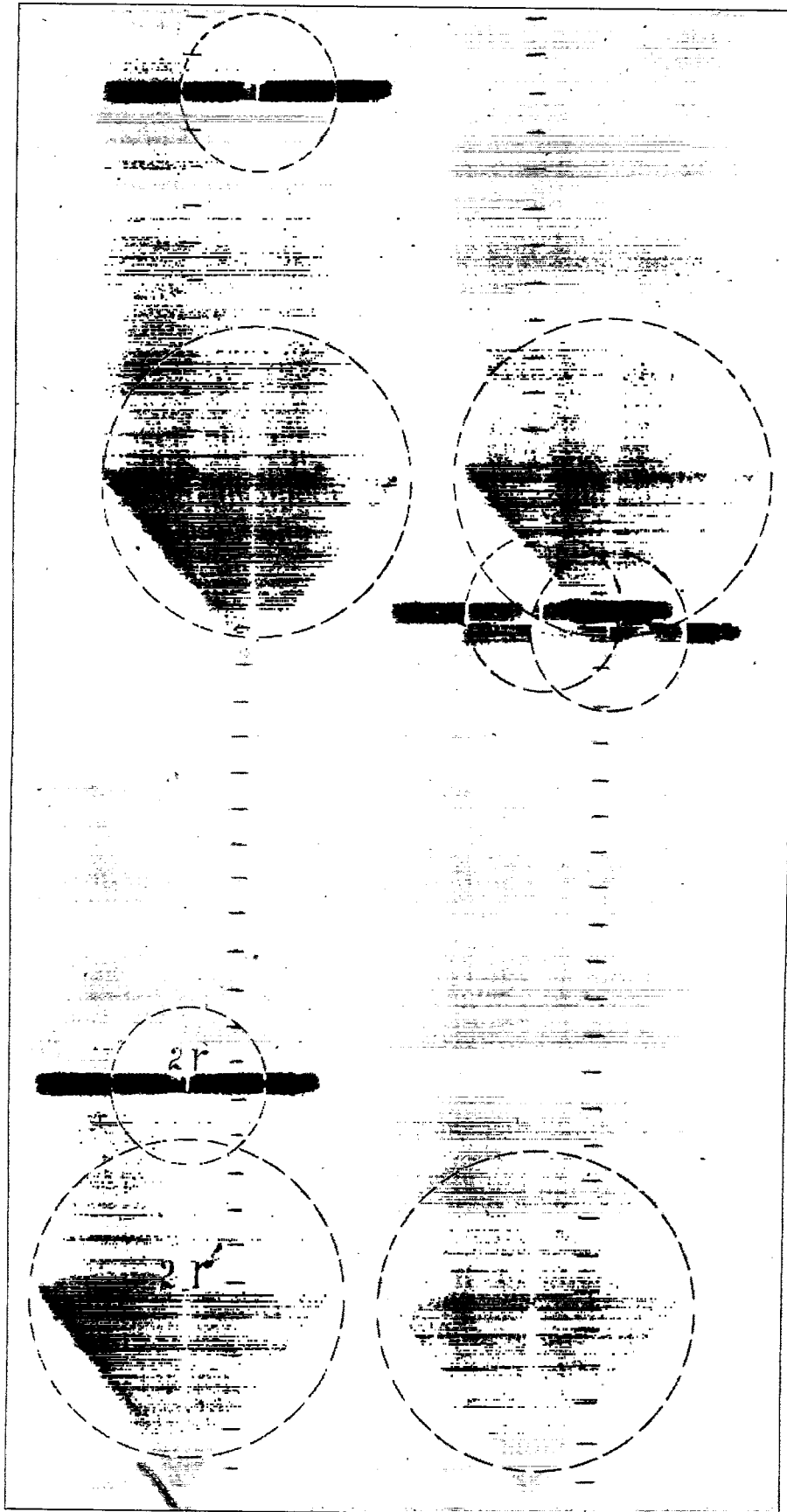


FIG. 1.—Shows a photographic time-volume record of four gaseous explosive reactions at constant pressure. The figures are $\frac{1}{2}$ actual size. $2r$ is the sphere of initial components considered. $2r'$ the sphere of its reaction products at the instant the reaction is complete

by expressing the initial and final condition of the reacting gases in terms of volume¹ at a constant pressure instead of pressure at a constant volume.

Besides the advantages attending the use of constant pressure methods as applied to thermodynamic studies of gaseous explosive reactions, the constant pressure bomb also offers unusual advantage in the study of an important kinetic phase of the reaction, namely, the rate at which the zone of explosive reaction is propagated within the active gases. The reason for this advantage both to thermodynamic and kinetic studies lies chiefly in the fact that at constant pressure the processes of the explosive reaction become automatically uniform, whereas, under the condition of constant volume and, to a much greater extent under conditions that only approach constant volume, they become unusually variable and complex. The possibility secured by a constant pressure bomb of so conditioning the reaction that it may run its course at a constant pressure (not necessarily atmospheric) thus greatly simplifies the course automatically taken by the transformation by eliminating a number of variables due to the effect of variable pressure upon the mass movement of the gases and upon their concentrations. The constant pressure bomb being transparent permits an accurate and continuous time-volume record of the reaction to be directly secured by photographic means. Such a record much reduced is shown at Figure 1. It gives the dimensions of the initial and final volumes of the reacting gases independent of the volume of the container and records the uniform progress by which a sphere r of initial components is transformed at a constant pressure into a sphere of equilibrium products, r' . This final volume represented by r' ,—as does the final pressure in the case of a constant volume bomb—corresponds to the equilibrium constant of the reaction,

$$K = \frac{[A]^{n'_1}[B]^{n'_2}[C]^{n'_3} \dots}{[A]^{n_1}[B]^{n_2}[C]^{n_3} \dots} \quad (2)$$

Pier has shown (Reference 1, p. 538) that the deviation from this constant due to the presence of an inert gas, permits the specific heat of that gas to be determined at the reaction temperature; and Siegel (Reference 3, p. 654), has shown that this expression allows the degree of dissociation of the combustion products to be found. For the case of the trimolecular reaction $2\text{CO} + \text{O}_2$, equation (2) may be written

$$K = \frac{[\text{CO}_2]^2}{[\text{CO}]^2[\text{O}_2]}$$

and if x is the degree of dissociation of CO_2 , then, for the case of the constant pressure bomb,

$$K_p = \frac{[\text{CO}_2]^2}{[\text{CO}]^2[\text{O}_2]} = \frac{(1-x)^2(2-x)}{x^3} \quad (3)$$

KINETICS

The photographic record (fig. 1) of the gross mechanism and progress of the reaction at constant pressure, upon which equal time intervals have been impressed, is a time-volume record of the reaction and hence may provide some general information as to the kinetics of the explosive transformation.

If the rate of flame movement is to be connected in any way with the rate of molecular transformation, it is obvious that its rate should be determined relative to the gases it is transforming and not relative to space, as is usually done. And it should likewise be recognized that

¹ It should be made clear that the term volume does not here refer to the actual volume of the temporary soap film container. The symmetry automatically assumed by the zone of reaction in the case of a homogeneous mixture of explosive gases fired from a point and under conditions of constant pressure, offers a much more accurate mode of procedure; for under these conditions the zone of reaction originating at the point of ignition advances in all directions from this point at a constant rate. It thus forms an expanding spherical shell of flame inclosing the products of combustion as they are formed by the passage of the initial active components through the zone of explosive reaction advancing at a constant rate. This sphere of reaction products is thus protected as well as may be from heat losses, during the reaction, due to conduction and convection. By reference to Figure 1 it will thus be seen that the initial volume of gases considered, is the volume of an ideal sphere $2r$ of the gases held by the temporary container, and not the volume of the container itself, for this is never a sphere. The final volume is the volume of the sphere $2r$ transformed into the sphere of reaction products, $2r'$. The conditions that determine uniform flame movement in a gaseous explosive reaction—whether for the slower reaction rates or for the more rapid rates of the explosive wave—are a homogeneous mixture of the explosive gases and a constant pressure; for under these conditions only is it possible for the mass movement of the gases and for their concentrations to remain constant during the reaction process.

unless the method employed makes it possible to follow the concentrations of the active gases which the zone of explosive reaction is entering, a kinetic relation connecting the movement of this region with the composition and concentration of the explosive gases, could hardly be expected to result from its use.

An examination of a great number of records similar to that shown at Figure 1, obtained with different gases at different concentration ratios, has shown that at constant pressure the rate of movement s of the zone of reaction, measured relative to the active gases, is proportional to the product of the initial partial pressures of those gases:

$$s = k_1 [A]^{n_1} [B]^{n_2} [C]^{n_3} \dots \dots \dots \quad (4)$$

In this expression, k_1 is a proportionality factor. The inclosed symbols refer to initial concentrations or partial pressures of the active components. s is the rate of propagation of the zone of reaction measured relative to the active gases it is entering.

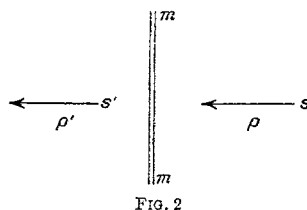
It was of interest to examine the effect of inert gases on the rate of propagation of the zone of reaction in the light of the kinetic relation expressed in (4) and by a method suggested by that employed in the determination of their effect upon the thermodynamic equilibrium. It is the purpose of this report to record the results obtained in this endeavor.

EXPERIMENTAL PART

From the photographic figure of the progress of the reaction, it will be seen that the constant rate of flame movement s' , *in space*, may be determined at any instant during the transformation. At the instant the reaction is completed its value may be written

$$s' = \frac{r'}{t}$$

But this is not the rate at which the flame is entering the gases. The rate s , at which the flame is entering the gases, may be found for the case of a spherical shell of flame expanding at a uniform rate s' , as follows: Let m , m (fig. 2) be an element of the flame surface held at rest by the uniform rate of flow s , of the active gases against it; then s will be the rate at which the flame area enters the gases and s' will be the rate at which the transformed gases leave the flame area. If ρ and ρ' are the initial and final gas densities then from the equality of masses



$$\rho s = \rho' s'$$

For the case of the two spheres of radius r and r' , we also have from the equality of masses

$$\frac{4}{3}\pi \rho r^3 = \frac{4}{3}\pi \rho' r'^3;$$

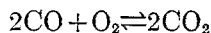
hence

$$\frac{s}{r^3} = \frac{s'}{r'^3}$$

and

$$s = s' \frac{r'^3}{r^3} = \frac{r'^3}{r'^2 t} \quad (5)$$

For experimental purposes, the gaseous explosive reaction at water vapor saturation,



was selected. For this special case equation (4) may be written

$$s = k_1 [\text{CO}]^2 [\text{O}_2] \quad (6)$$

and including equation (5),

$$s = \frac{r'^3}{r'^2 t} = k_1 [\text{CO}]^2 [\text{O}_2] \quad (7)$$

Since the sum of the partial pressures of the gaseous components present in the reaction at pressure p must equal p , equation (6) may be written for atmospheric pressure,

$$s = k_1 [\text{CO}]^2 [1 - \text{CO}]$$

without designating the composition of $1 - \text{CO}$ further than to indicate that the sum of the partial pressures of its components remains the same as the partial pressure of the component O_2 in equation (6) and that under the same circumstances both equations represent the same impact probability though not the same proportion of effective impacts nor the same potential energy. In case the component $1 - \text{CO}$ is made up of the fraction a of the active gas O_2 and the fraction $(1 - a)$ of an inactive gas, the partial pressure of this component may be expressed as

$$[1 - \text{CO}] = \underset{\text{active}}{[1 - \text{CO}] a} + \underset{\text{inert}}{[1 - \text{CO}] (1 - a)}$$

and equation (6) may then be written as

$$s = k_1 ([\text{CO}]^2 [1 - \text{CO}] a + [\text{CO}]^2 [1 - \text{CO}] (1 - a)).$$

If all of the impacts involving the inert gas are futile and the possible effect of its various physical properties as specific heat, heat conductivity, etc., on the course of a thermal reaction be disregarded, then the last term in the above expression may be neglected and the effect on reaction probability of replacing the fraction $(1 - a)$ of an active gas by an inactive one may be written

$$s = k_1 [\text{CO}]^2 [1 - \text{CO}] a \quad (8)$$

This mass law expression takes into account the effect of the remaining active components only; and this is the major effect to be expected; but while the inert gas introduced may take no part in the molecular transformation, its presence in the zone of explosive reaction and in the active gases adjacent to it, must necessarily affect the heat distribution in that region. If the effect of the thermal properties of the inert gas is a simple function of its concentration, then the deviation from the relation expressed in (8), due to its presence in the zone of reaction might be expressed as

$$s = \frac{r^3}{r'^2 t} = k_1 [\text{CO}]^2 [1 - \text{CO}] a + \beta [1 - \text{CO}] (1 - a). \quad (9)$$

From this relationship it will be seen that the maximum effect of the inert gas should be found for the minimum value of $[\text{CO}]$ and *vice versa*. In carrying out the observations, therefore, the effect of each successive increase in the partial pressure of each of the inert gases investigated, nitrogen, carbon dioxide, and helium,² was observed over the entire range of partial pressure ratios that would ignite. This procedure, which resulted in a very large number of observations and calculations, was necessary because the proportion of inert gas to the whole varies with each ratio of the partial pressures.

² Some of the thermal properties of the gases involved in the reaction are given in the following table:

Gas	C_p	Heat conductivity
N_2	6.75	566
CO_2	9.44	337
He	5.00	3,360
CO	6.75	542
O_2	6.75	570

For the purpose of comparison, Table I gives the results obtained when no inert gas was present:

TABLE I
FLAME SPEED AND VELOCITY COEFFICIENT FOR THE $2\text{CO} + \text{O}_2$ REACTION WITHOUT INERT GAS

Partial pressure (atmospheres)		$T = [\text{CO}]^2 [\text{O}_2]$	$s = \frac{r}{T^{1/2}}$ cm/sec.	$k_1 = \frac{s}{[\text{CO}]^2 [\text{O}_2]}$
[CO]	[O ₂]			
0.25	0.75	0.0469	34.9	745
.30	.70	.0630	44.0	698
.35	.65	.0796	53.5	672
.39	.61	.0907	66.0	711
.435	.565	.1069	75.5	706
.45	.55	.1114	76.0	682
.47	.53	.1171	83.5	713
.48	.52	.1198	84.0	701
.50	.50	.1250	87.0	696
.505	.495	.1262	88.0	681
.532	.468	.1326	89.0	672
.55	.45	.1361	94.0	691
.56	.44	.1380	93.0	674
.585	.415	.1420	97.5	687
.60	.400	.1440	99.5	691
.61	.39	.1451	100.0	689
.63	.37	.1468	102.0	695
.67	.33	.1481	104.0	702
.69	.31	.1476	104.0	705
.70	.30	.1470	99.1	674
.75	.25	.1406	96.3	685
.80	.20	.1280	90.5	707
.825	.175	.1191	82.0	693
.84	.16	.1129	78.7	697
.86	.14	.1136	66.5	642
.894	.106	.1147	58.0	685
.94	.06	.0530	33.0	622
				Av. k_1 690

The results given in the above table may be expressed in graphic form by plotting the values of s as ordinates and either the corresponding partial pressures or the corresponding values for impact probability, $T = [\text{CO}]^2 [\text{O}_2]$, as abscissas. In Figure 3 and in the other figures to be given, the more familiar relation between rates and partial pressures will be used. The experimental values of s found are represented in Figure 3 by solid circles. Theoretical values corresponding to the relation $s = k_1 [\text{CO}]^2 [\text{O}_2]$ are represented by open circles connected by a continuous line. This curve will be reproduced for reference in the figures that follow that represent the effect of an inert gas on the rate of reaction.

In Figure 4 the upper curve represents results when no inert gas is present. The lower curve represented by a continuous line corresponds to equation (8), $s = k_1 [\text{CO}]^2 [1 - \text{CO}]^{0.9}$, for the case where 10 per cent of the component $1 - \text{CO}$ is made up of an inert gas. The experimental values found when 10 per cent of inert gas used was N_2 are indicated by the mark \times ; when the inert gas was CO_2 by the mark \blacksquare ; and when the inert gas was He by the mark \blacktriangle . When such small amounts as 10 per cent of the different inert gases are introduced, not much difference in their effect is to be noticed. Their thermal characteristics do not mask the effect of the active gases.

In like manner, Figure 5 represents results obtained when 20 per cent of the component $1 - \text{CO}$ consists of an inert gas. The lower continuous curve corresponds to equation (8) for this case, $s = k_1 [\text{CO}]^2 [1 - \text{CO}]^{.8}$. The observed values when this amount of the three inert gases N_2 , CO_2 , and He were successively used are indicated by the same symbols employed in Figure 4.

When 40 per cent of the component $1 - \text{CO}$ consists of an inert gas, the individual thermal characteristics of the different gases become more marked. When a somewhat greater amount than 40 per cent of CO_2 is employed at atmospheric pressure the range of ignition is much

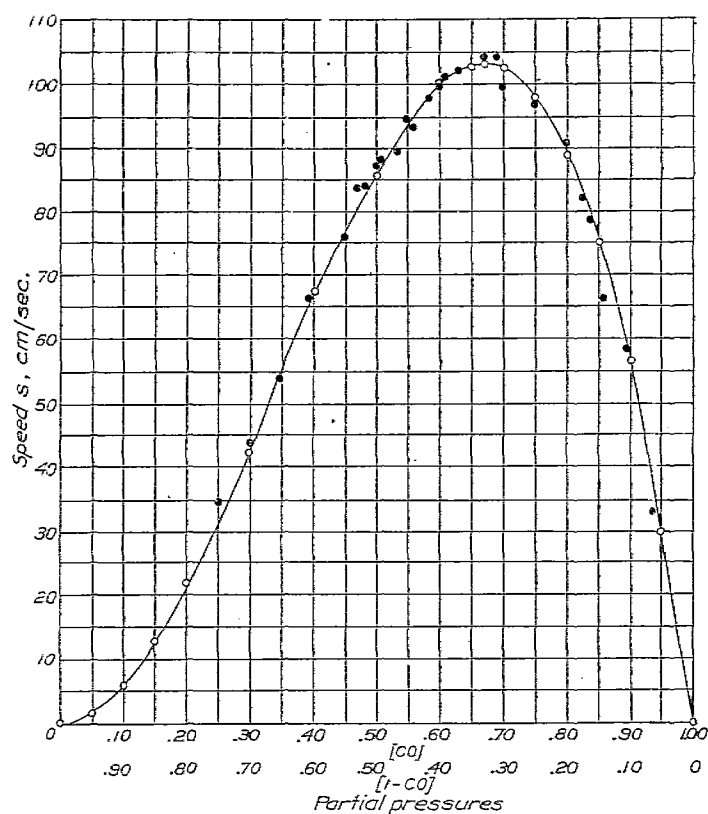


FIG. 3.—Shows the relation between the linear rate of propagation of the zone of reaction, relative to the active gases, and the partial pressures, $[]$, of those gases, CO and O_2 . The solid circles are the observed values, $s = \frac{r^2}{t}$. The open circles, and the continuous line show calculated values, $s = k_1 [CO]^2 [O_2]$

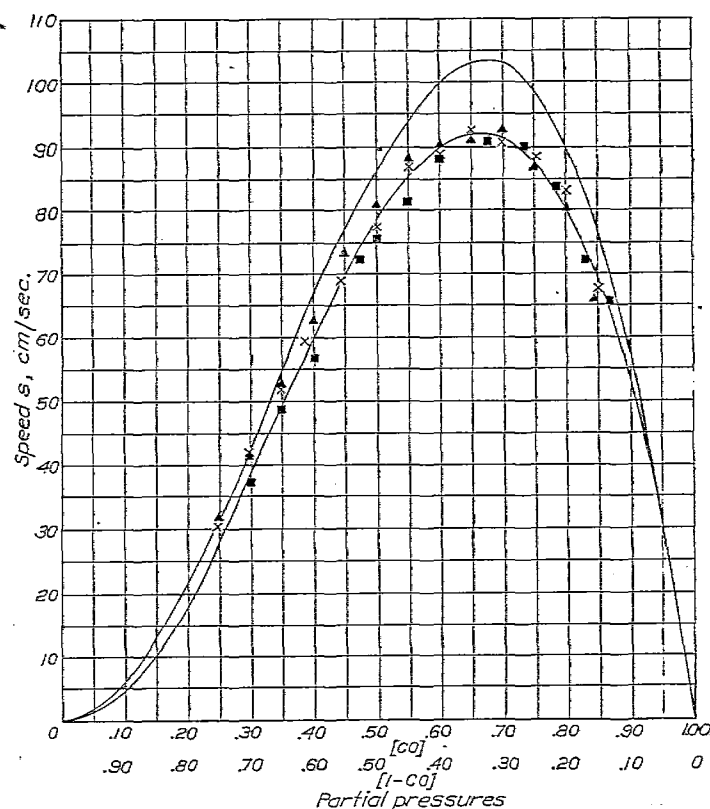


FIG. 4.—The upper curve corresponds to values found when no inert gas was present. The lower continuous curve corresponds to equation (3) for the case where 10% of the component +1-CO consists of an inert gas: $s = k_1 [CO]^2 [1-CO].9$. The observed values when the inert gas used was N_2 are indicated by the mark X, CO_2 by the mark ■, and He by the mark ▲

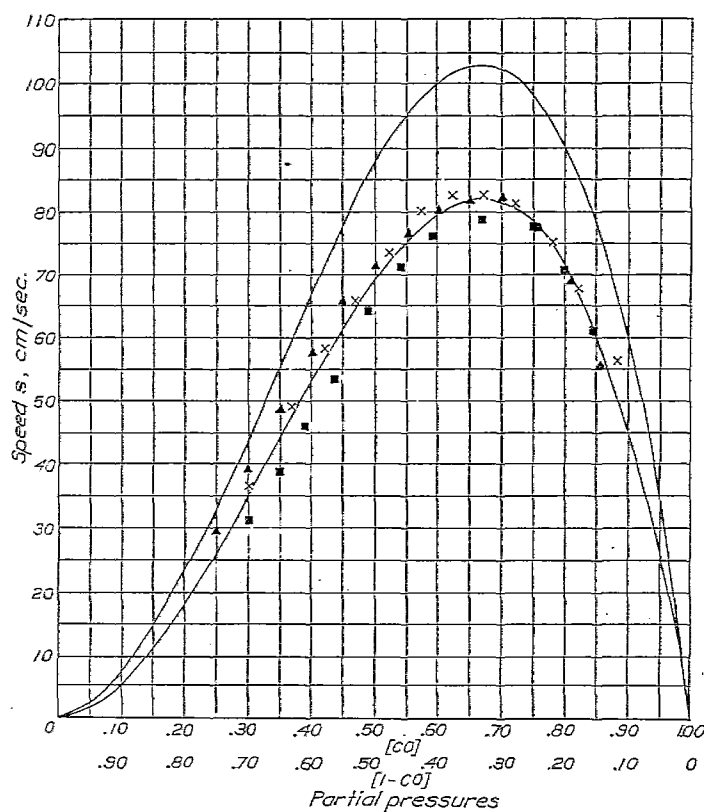


FIG. 5.—The upper curve corresponds to values found the lower continuous curve corresponds to equation the component +1-CO consists of an inert gas: $s =$ served values when the inert gas used was N_2 are indicated by the mark X, CO_2 by the mark ■, and He by the mark ▲

reduced and the reaction rate becomes so slow that the few results obtainable with the gas are of little value—the sphere of heated reaction products starts to rise, like a hot-air balloon before the reaction is completed.

A tabulation of the results obtained with 40 per cent He is given below in Table II. Similar tabulations were made in all cases for the other inert gases used and for each successive increase in the amount introduced.

TABLE II

FLAME SPEED AND CONSTANT β FOR THE $2\text{CO} + \text{O}_2$ REACTION IN THE PRESENCE OF HELIUM

Partial pressure (atmospheres) [CO] [1-CO] [He]			$\Gamma = \frac{r}{[CO]^2[1-CO]}$	$s' = \frac{r'}{t}$ cm/sec.	$s = s' \frac{r^2}{r'^2}$ cm/sec.	s cm/sec.	$\beta = \frac{s - k_{10} [CO]^2 [1-CO]}{[He]}$
0.22	0.78	0.312	0.0377	256	48.3		
				266	50.2		
				267	50.4		
				261	49.2	49.5	112
.265	.735	.294	.0516	335	55.5		
				349	57.9		
				340	56.3		
				330	54.6	56.1	119
.30	.70	.280	.0630	368	58.6		
				393	62.7		
				359	57.1		
				384	61.2	59.9	119
.35	.65	.260	.0796	440	60.0		
				455	62.8		
				441	60.2		
				459	62.6	61.4	111
.40	.60	.240	.0960	512	70.0		
				470	64.3		
				498	68.0		
				511	69.8	68.0	117
.45	.55	.220	.1140	548	72.8		
				552	73.3		
				553	73.4		
				509	67.6	71.8	118
.50	.50	.200	.1250	566	72.1		
				563	71.7		
				573	73.0	72.3	99
.55	.45	.180	.1360	671	80.5		
				626	75.2		
				615	73.8		
				613	73.6	75.8	105
.60	.40	.160	.1440	635	79.1		
				590	73.6		
				610	76.1		
				618	77.0	76.5	101
.65	.35	.140	.1480	619	77.6		
				604	75.7		
				618	77.5		
				605	75.9	76.6	103
.70	.30	.120	.1470	588	73.5		
				591	73.9		
				582	72.8		
				604	75.5	73.9	108
.75	.25	.100	.1410	560	72.4		
				538	69.5		
				536	69.2		
				518	66.9	69.5	103
.80	.20	.080	.1280	480	69.1		
				439	62.5		
				421	59.8		
				445	61.9	63.3	104
.85	.15	.060	.1080	291	50.7		
				299	52.0		
				314	55.5		
				287	50.0	52.0	100
							Av. β 108

Figure 6 shows experimental results obtained when 40 per cent of the component 1-CO was made up of inert gas. The lower continuous curve corresponds to equation (8) for this case, $s = k_1 [\text{CO}]^2 [\text{O}_2] .6$. The deviations of the experimental values from this curve are well marked.

In the last column of Table II for helium is given the experimental value of β in equation (9).

$$\beta = \frac{s - k_1 a [\text{CO}]^2 [1 - \text{CO}]}{[\text{He}]}$$

When the average value of this factor, 108, is introduced into equation (9) and the values of s computed over the possible range of partial pressure ratios, the curve marked He results. In the same way there was obtained from the experimental values for 40 per cent CO_2 , $\beta = -41.8$ and for 40 per cent N_2 , $\beta = 42$. When these values are substituted in equation (9) the curves marked CO_2 and N_2 are determined. The constancy of these β -values indicate that the thermal effect of the inert gas on the rate of flame propagation is proportional to its concentration in the explosive mixture. That its value depends upon the additive effect its physical properties have on the heat distribution of the reaction seems reasonable. Of these properties, that of heat conductivity is expressible as a rate; that of its specific heat, being a thermodynamic factor, is expressible, as already pointed out (Reference 4) in terms of the thermodynamic equilibrium. The kinetic effect of the specific heat of the inert gas would be expressed as a temperature coefficient of the velocity constant k (Reference 6).

The effect of adding an inert gas of high heat conductivity to a gaseous explosive mixture may seem in some cases anomalous, for it may even increase the rate of flame propagation for some partial pressure ratios above those where no inert gas is present.

This may be seen by comparing the observed and theoretical values for the 40 per cent He mixtures with the observed and theoretical values for pure CO and O_2 mixtures. The presence of an inert gas of high heat conductivity also increases markedly the range of ignition; while a gas of low conductivity reduces it.

The mixture ratio for maximum flame velocity for the conditions expressed by equations (6) and (8) is the point 0.66+ in the coordinate figures. But for equation (9) this point will be displaced to the left according to the positive magnitude of the last term, and to the right according to its negative magnitude. It will be seen that the experimental result confirms this deduction.

It is also of interest to note that it is possible to secure a mixture of two inert gases whose thermal effect upon the rate of reaction is in opposite sense, such that their effects balance each other and the last term in equation (9) becomes negligible. The conclusion could be

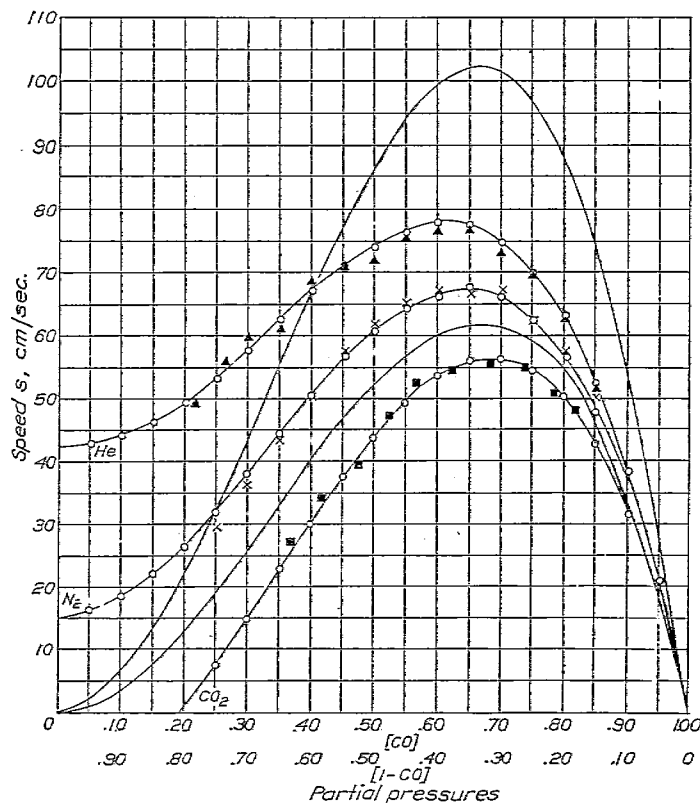


FIG. 6.—The upper curve corresponds to values found when no inert gas was present; the lower heavy continuous curve without other marks corresponds to equation (8) for the case where 40% of the component 1-CO consists of an inert gas: $s = k_1 [\text{CO}]^2 [1 - \text{CO}] .6$. The curves marked He, N_2 and CO_2 represented by the open circles and the solid line correspond to equation (9) when the respective experimental values for β are introduced. The observed values when the inert gas used was N_2 are indicated by the mark X, CO_2 by the mark ■, and He by the mark ▲.

drawn from such a case that the reaction velocity is dependent only on the concentrations of the active components. This conclusion might also seem warranted by the experimental results obtained when the inert gas is present in comparatively small amounts; Figures 4 and 5; and for all of the results where the value of $[CO]$ is large and the partial pressure of the inert gas small. It was therefore important to make use of inert gases whose thermal characteristics differed widely and to determine in each case the effect of the reaction of the same active components upon the same partial pressure of each of the inert gases and this for the inert gases over the entire range of partial pressure mixtures that would ignite. The complete tabulation of so large a number of observations is perhaps unnecessary to reproduce here. A specimen tabulation for 40 per cent He is given, Table II. The theoretical and observed results obtained for that gas and for CO_2 and N_2 are indicated graphically at Figure 6.

BUREAU OF STANDARDS,
WASHINGTON, D. C., *June 24, 1927.*

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